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(54) Title: HIGH EFFICIENCY DELIVERY SYSTEM COMPRISING ZEOLITES (57) Abstract Laundry particles comprising: a) a porous carrier selected from the group consisting of Zeolite X, Zeolite Y, and mixtures thereof; and b) laundry agents comprising from about 5 % to about 100 % by weight of deliverable agents, preferably comprising from about 0.1 % to about 50 % blocker agents.		

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HIGH EFFICIENCY DELIVERY SYSTEM COMPRISING ZEOLITES

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FIELD OF THE INVENTION

The present invention relates to laundry particles, especially for delivery of perfume agents, and detergent compositions comprising these laundry particles, especially granular detergents.

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BACKGROUND OF THE INVENTION

Most consumers have come to expect scented laundry products and to expect that fabrics which have been laundered also to have a pleasing fragrance. Perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carryover from an aqueous laundry bath onto fabrics is often marginal. Industry, therefore, has long searched for an effective perfume delivery system for use in laundry products which provides long-lasting, storage-stable fragrance to the product, as well as fragrance to the laundered fabrics.

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Laundry and other fabric care compositions which contain perfume mixed with or sprayed onto the compositions are well known from commercial practice. Because perfumes are made of a combination of volatile compounds, perfume can be continuously emitted from simple solutions and dry mixes to which the perfume has been added. Various techniques have been developed to hinder or delay the release of perfume from compositions so that they will remain aesthetically pleasing for a longer length of time. To date, however, few of the methods deliver significant fabric odor benefits after prolonged storage of the product.

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Moreover, there has been a continuing search for methods and compositions which will effectively and efficiently deliver perfume from a laundry bath onto fabric surfaces. As can be seen from the following disclosures, various methods of perfume delivery have been developed involving protection of the perfume through the wash cycle, with release of the perfume onto fabrics. U.S. Pat. 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents, including perfume, through the wash and dry cycle via a fatty quaternary ammonium salt. U.S. Pat. 4,402,856, Schnoring et al.

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issued Sept. 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell material which will allow for diffusion of perfume out of the capsule only at certain temperatures. U.S. Pat. 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into waxy particles to protect the perfume
5 through storage in dry compositions and through the laundry process. The perfume assertedly diffuses through the wax on the fabric in the dryer. U.S. Pat. 5,066,419, Walley et al, issued Nov. 19, 1991, teaches perfume dispersed with a water-insoluble nonpolymeric carrier material and encapsulated in a protective shell by coating with a water-insoluble friable coating material. U.S. Pat.
10 5,094,761, Trinh et al, issued Mar. 10, 1992, teaches a perfume/cyclodextrin complex protected by clay which provides perfume benefits to at least partially wetted fabrics.

Another method for delivery of perfume in the wash cycle involves combining the perfume with an emulsifier and water-soluble polymer, forming
15 the mixture into particles, and adding them to a laundry composition, as is described in U.S. Pat. 4,209,417, Whyte, issued June 24, 1980; U.S. Pat. 4,339,356, Whyte, issued July 13, 1982; and U.S. Pat. No. 3,576,760, Gould et al, issued April 27, 1971. However, even with the substantial work done by industry
20 in this area, a need still exists for a simple, more efficient and effective perfume delivery system which can be mixed with laundry compositions to provide initial and lasting perfume benefits to fabrics which have been treated with the laundry product.

The perfume can also be adsorbed onto a porous carrier material, such as a polymeric material, as described in U.K. Pat. Pub. 2,066,839, Bares et al,
25 published July 15, 1981. Perfumes have also been adsorbed onto a clay or zeolite material which is then admixed into particulate detergent compositions. Generally, the preferred zeolites have been Type A or 4A Zeolites with a nominal pore size of approximately 4 Angstrom units. It is now believed that with Zeolite A or 4A, the perfume is adsorbed onto the zeolite surface with relatively little of
30 the perfume actually absorbing into the zeolite pores. While the adsorption of perfume onto zeolite or polymeric carriers may perhaps provide some improvement over the addition of neat perfume admixed with detergent compositions, industry is still searching for improvements in the length of storage time of the laundry compositions without loss of perfume characteristics, in the
35 intensity or amount of fragrance delivered to fabrics, and in the duration of the perfume scent on the treated fabric surfaces.

Combinations of perfumes generally with larger pore size zeolites X and Y are also taught in the art. East German Patent Publication No. 248,508, published August 12, 1987 relates to perfume dispensers (e.g., an air freshener) containing a faujasite-type zeolite (e.g., zeolite X and Y) loaded with perfumes. The critical
5 molecular diameters of the perfume molecules are said to be between 2-8 Angstroms. Also, East German Patent Publication No. 137,599, published September 12, 1979 teaches compositions for use in powdered washing agents to provide thermoregulated release of perfume. Zeolites A, X and Y are taught for use in these compositions. These earlier teachings are repeated in the more
10 recently filed European applications Publication No. 535,942, published April 7, 1993, and Publication No. 536,942, published April 14, 1993, by Unilever PLC, and U.S. Patent 5,336,665, issued August 9, 1994 to Garner-Gray et al.

Effective perfume delivery compositions are taught by WO 94/28107, published December 8, 1994 by The Procter & Gamble Company. These
15 compositions comprise zeolites having pore size of at least 6 Angstroms (e.g., Zeolite X or Y), perfume releaseably incorporated in the pores of the zeolite, and a matrix coated on the perfumed zeolite comprising a water-soluble (wash removable) composition in which the perfume is substantially insoluble, comprising from 0% to about 80%, by weight, of at least one solid polyol
20 containing more than 3 hydroxyl moieties and from about 20% to about 100%, by weight, of a fluid diol or polyol in which the perfume is substantially insoluble and in which the solid polyol is substantially soluble.

Another problem in providing perfumed products is the odor intensity associated with the products, especially high density granular detergent
25 compositions. As the density and concentration of the detergent composition increase, the odor from the perfume components can become undesirably intense. A need therefore exists for a perfume delivery system which substantially releases the perfume odor during use and thereafter from the dry fabric, but which does not provide an overly- intensive odor to the product itself.

30 By the present invention it has now been discovered that certain agents, preferably perfume agents, can be selected based on specific selection criteria to maximize impact during and/or after the wash process, while minimizing the amount of agents needed in total to achieve a consumer noticable result. Such compositions are desirable not only for their consumer noticable benefits (e.g.,
35 odor aesthetics), but also for their potentially reduced cost through effiecent use of lesser amounts of ingredients.

The present invention solves the long-standing need for a simple, effective, storage-stable delivery system which provides benefits (especially fabric odor benefits) during and after the laundering process. Further, perfume-containing compositions have reduced product odor during storage of the composition. The present invention also provides the additional benefit of continued odor release from laundered fabrics when exposed to heat or humidity while being stored, dried or ironed.

BACKGROUND ART

U.S. Patent 4,539,135, Ramachandran et al, issued September 3, 1985, discloses particulate laundry compounds comprising a clay or zeolite material carrying perfume. U.S. Patent 4,713,193, Tai, issued December 15, 1987, discloses a free-flowing particulate detergent additive comprising a liquid or oily adjunct with a zeolite material. Japanese Patent HEI 4[1992]-218583, Nishishiro, published August 10, 1992, discloses controlled-release materials including perfumes plus zeolites. U.S. Patent 4,304,675, Corey et al, issued December 8, 1981, teaches a method and composition comprising zeolites for deodorizing articles. East German Patent Publication No. 248,508, published August 12, 1987; East German Patent Publication No. 137,599, published September 12, 1979; European applications Publication No. 535,942, published April 7, 1993, and Publication No. 536,942, published April 14, 1993, by Unilever PLC; U.S. Patent 5,336,665, issued August 9, 1994 to Garner-Gray et al.; and WO 94/28107, published December 8, 1994.

SUMMARY OF THE INVENTION

The present invention relates to a laundry particle comprising:

- a) a porous carrier selected from the group consisting of Zeolite X, Zeolite Y, and mixtures thereof; and
- b) laundry agents comprising from about 5% to about 100% by weight of deliverable agents (preferably comprising from about 0.1% to about 50% blocker agents), except that said laundry agents do not comprise more than 6% of a mixture of non-deliverable agents containing at least 0.1% isobutyl quinoline, at least 1.5% galaxolide 50%, at least 0.5% musk xylol, at least 1.0% exaltex, and at least 2.5% patchouli oil.

The present invention further relates to laundry compositions comprising from about 0.01% to about 50% (preferably from about 0.01% to about 10%; more preferably from about 0.02% to about 1%) of a laundry particle according to the present invention and in total from about 40% to about 99.99% (preferably from

about 90% to about 99.99%; more preferably from about 99.0% to about 99.98%) of laundry ingredients selected from the group consisting of surfactants, builders, bleaching agents, enzymes, soil release polymers, dye transfer inhibitors, and mixtures thereof.

5 All percentages, ratios, and proportions herein are on a weight basis unless otherwise indicated. All documents cited are hereby incorporated by reference in their entirety.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph representing a plot of various laundry agents in a volume/surface area ratio vs. cross sectional area plane with the incorporation line and blocker line designated.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a delivery system comprising a dehydrated (preferably less than about 10% by weight desorbable water) Type X Zeolite, Type Y Zeolite, or a mixture thereof, wherein a laundry agent (preferably a perfume or a mixture of perfumes) has been absorbed in the pores of said zeolite. Further, such agents are not just random mixtures of agents as described by the prior art referenced hereinbefore for perfumes absorbed on these types of zeolites. Such compositions appear to simply attempt to use the same perfume mixtures that are otherwise commonly sprayed onto the laundry particles, thereby attempting to retain these mixtures by the association with these zeolite carriers.

By contrast, the present invention compositions dramatically limit the agents which are a part of the system adsorbed onto the zeolite particles based on specific selection criteria as described in detail hereinafter. Such selection criteria further allow the formulator to take advantage of interactions between these agents when incorporated into the zeolite pores to maximize consumer noticeable benefits while minimizing the quantities of agents utilized.

This is not to say that the mixture of agents cannot comprise some amount of agents which are incapable of being incorporated into the pores of the zeolite. Such agents may be and typically are present, but only to the extent that they do not substantially interfere with the incorporation of the agents selected for absorption into the zeolite pores. Such materials may be included in the mixture of laundry agents that comprises deliverable agents (as defined hereinafter) to be incorporated into the zeolite, but preferably are part of the laundry components added separately to the laundry composition. For example, preferred herein are laundry compositions which further contain perfume agents added to (typically by spraying on) the final laundry composition containing laundry particles according

to the present invention. Such additional perfume agents may be the same as the perfume agents incorporated into the zeolite, but preferably are a different but complementary perfume mixture.

The selection criteria are defined hereinafter which identify raw materials
5 and combinations that are useful according to the present invention. Especially desirable are combinations which interact to further delay release of the laundry agents from the zeolite, such as by including some level of blocker agents (as defined hereinafter).

While little is known in the literature about the exact location of guest
10 molecules in zeolite, a good body of work has developed around the diffusion of materials into zeolite's structured pores (J. Karger, D.M. Ruthven, "Diffusion in Zeolites", John Willey & Sons, New York, 1992). The primary factor that influences inclusion of a guest molecule into a zeolite pore is the size of the guest molecule relative to the zeolite pore opening. While zeolite pores have been well
15 characterized, perfume molecules are not traditionally defined by their size parameters; such are typically ignored by the prior art systems which sought to use zeolites as carriers, with the exception being the general size description relating to air freshener compositions contained in East German Patent Publication No. 248,508, published August 12, 1987.

20 However, for purposes of the present invention compositions exposed to the aqueous medium of the laundry wash process, several characteristic parameters of guest molecules are important to identify and define: their longest and widest measures; cross sectional area; molecular volume; and molecular surface area. These values are calculated for individual agents (e.g., individual perfume
25 molecules) using the CHEMX program (from Chemical Design, Ltd.) for molecules in a minimum energy conformation as determined by the standard geometry optimized in CHEMX and using standard atomic van der Waal radii. Definitions of the parameters are as follows:

"Longest": the greatest distance (in Angstroms) between atoms in the
30 molecule augmented by their van der Waal radii.

"Widest": the greatest distance (in Angstroms) between atoms in the molecule augmented by their van der Waal radii in the projection of the molecule on a plane perpendicular to the "longest" axis of the molecule.

"Cross Sectional Area": area (in square Angstrom units) filled by the
35 projection of the molecule in the plane perpendicular to the longest axis.

"Molecular Volume": the volume (in cubic Angstrom units) filled by the molecule in its minimum energy configuration.

"Molecular Surface Area": arbitrary units that scale as square Angstroms (for calibration purposes, the molecules methyl beta naphthyl ketone, benzyl salicylate, and camphor gum have surface areas measuring 128 ± 3 , 163.5 ± 3 , and 122.5 ± 3 units respectively).

- 5 The shape of the molecule is also important for incorporation. For example, a symmetric perfectly spherical molecule that is small enough to be included into the zeolite channels has no preferred orientation and is incorporated from any approach direction. However, for molecules that have a length that exceeds the pore dimension, there is a preferred "approach orientation" for inclusion.
- 10 Calculation of a molecule's volume/surface area ratio is used herein to express the "shape index" for a molecule. The higher the value, the more spherical the molecule.

- For purposes of the present invention, agents are classified according to their ability to be incorporated into zeolite pores, and hence their utility as
- 15 components for delivery from the zeolite carrier through an aqueous environment. Plotting these agents in a volume/surface area ratio vs. cross sectional area plane (see FIG 1) permits convenient classification of the agents in groups according to their incorporability into zeolite. In particular, for the zeolite X and Y carriers according to the present invention, agents are incorporated if they fall below the
- 20 line (herein referred to as the "incorporation line") defined by the equation:

$$y = -0.01068x + 1.497$$

- where x is cross sectional area and y is volume/surface area ratio. Agents that fall below the incorporation line are referred to herein as "deliverable agents"; those agents that fall above the line are referred to herein as "non-deliverable
- 25 agents".

- For containment through the wash, deliverable agents are retained in the zeolite carrier as a function of their affinity for the carrier relative to competing deliverable agents. Affinity is impacted by the molecule's size, hydrophobicity, functionality, volatility, etc., and can be effected via interaction between
- 30 deliverable agents within the zeolite carrier. These interactions permit improved through the wash containment for the deliverable agents mixture incorporated. Specifically, for the present invention, the use of deliverable agents having at least one dimension that is closely matched to the zeolite carrier pore dimension slows the loss of other deliverable agents in the aqueous wash environment. Deliverable
- 35 agents that function in this manner are referred to herein as "blocker agents", and are defined herein in the volume/surface area ratio vs. cross sectional area plane as those deliverable agent molecules falling below the "incorporation line" (as

defined hereinbefore) but above the line (herein referred to as the "blocker line") defined by the equation:

$$y = -0.01325x + 1.46$$

where x is cross sectional area and y is volume/surface area ratio.

5 For the present invention compositions which utilize zeolite X and Y as the carriers, all deliverable agents below the "incorporation line" can be delivered and released from the present invention compositions, with the preferred materials being those falling below the "blocker line". Also preferred are mixtures of blocker agents and other deliverable agents. Laundry agents mixtures useful for
10 the present invention laundry particles preferably comprise from about 5% to about 100% (preferably from about 25% to about 100%; more preferably from about 50% to about 100%) deliverable agents (except that said laundry agents do not comprise more than 6% of a mixture of non-deliverable agents containing at least 0.1% isobutyl quinoline, at least 1.5% galaxolide 50%, at least 0.5% musk
15 xylol, at least 1.0% exaltex, and at least 2.5% patchouli oil) and preferably comprising from about 0.1% to about 100% (preferably from about 0.1% to about 50%) blocker agents, by weight of the laundry agents mixture.

Obviously for the present invention compositions whereby perfume agents are being delivered by the compositions, sensory perception is required for a
20 benefit to be seen by the consumer. For the present invention perfume compositions, the most preferred perfume agents useful herein have a threshold of noticability (measured as odor detection thresholds ("ODT") under carefully controlled GC conditions as described in detail hereinafter) less than or equal to 10 parts per billion ("ppb"). Agents with ODTs between 10 ppb and 1 part per
25 million ("ppm") are less preferred. Agents with ODTs above 1 ppm are preferably avoided. Laundry agent perfume mixtures useful for the present invention laundry particles preferably comprise from about 0% to about 80% of deliverable agents with ODTs between 10 ppb and 1 ppm, and from about 20% to about 100% (preferably from about 30% to about 100%; more preferably from about 50% to
30 about 100%) of deliverable agents with ODTs less than or equal to 10 ppb.

Also preferred are perfumes carried through the laundry process and thereafter released into the air around the dried fabrics (e.g., such as the space around the fabric during storage). This requires movement of the perfume out of the zeolite pores with subsequent partitioning into the air around the fabric. Preferred
35 perfume agents are therefore further identified on the basis of their volatility. Boiling point is used herein as a measure of volatility and preferred materials have a boiling point less than 300 C. Laundry agent perfume mixtures useful for the

present invention laundry particles preferably comprise at least about 50% of deliverable agents with boiling point less than 300 C (preferably at least about 60%; more preferably at least about 70%).

In addition, preferred laundry particles herein comprise compositions wherein at least about 80%, and more preferably at least about 90%, of the deliverable agents have a "ClogP value" greater than about 1.0. ClogP values are obtained as follows.

Calculation of ClogP:

These perfume ingredients are characterized by their octanol/water partition coefficient P. The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentration in octanol and in water. Since the partition coefficients of most perfume ingredients are large, they are more conveniently given in the form of their logarithm to the base 10, logP.

The logP of many perfume ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), contains many, along with citations to the original literature.

However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P.G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990). The fragment approach is based on the chemical structure of each perfume ingredient and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, can be used instead of the experimental logP values in the selection of perfume ingredients.

Determination of Odor Detection Thresholds:

The gas chromatograph is characterized to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.2 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine whether a material has a threshold below 10 ppb, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC

effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability.

The necessary amount of analyte is injected onto the column to achieve a 10 ppb concentration at the detector. Typical gas chromatograph parameters for
5 determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

10 Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute

15 Inlet Temp. 245°C

Detector Temp. 285°C

Temperature Information

Initial Temperature: 50°C

Rate: 5C/minute

20 Final Temperature: 280°C

Final Time: 6 minutes

Leading assumptions: 0.02 minutes per sniff

GC air adds to sample dilution

The component materials are described below.

25 Laundry Agents

As used herein, the term "laundry agents" refers to any material useful in laundry detergent compositions of which some of the molecules have the hereinbefore required properties for incorporation into the zeolite X or Y carriers for the present invention laundry particles. For example, agents may be selected
30 from those materials which are perfumes, insect repellents, antimicrobial agents, bleach activators, etc.

A wide variety of chemicals are known for perfume uses, including materials such as aldehydes, ketones and esters. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of
35 various chemical components are known for use as perfumes. The perfumes herein can be relatively simple in their compositions or can comprise highly sophisticated complex mixtures of natural and synthetic chemical components, all

chosen to provide any desired odor within the selection criteria defined hereinbefore.

Typical perfume agents which are deliverable agents useful for the present invention compositions, alone or in any combination as desired for the odor impression being sought, include but are not limited to the following.

1. Blocker Agents:

<u>Agents</u>	<u>ODT\leq10ppb</u>	<u>BP$<$300°C</u>	<u>ClogP$>$1.0</u>
LRG 201	--	--	Yes
10 dimethyl benzyl carbinyl acetate	No	--	
Yes			
terpinyl acetate	--	--	Yes
cyclohexyl salicylate	--	--	Yes
camphor gum	--	Yes	Yes
15 benzyl salicylate	Yes	--	Yes
citrowanil b	--	--	Yes
flor acetate	Yes	--	Yes
iso bornyl cyclohexanol	--	--	--
verdox	No	--	Yes

20

2. Other Deliverable Agents:

<u>Agents</u>	<u>ODT\leq10ppb</u>	<u>BP$<$300°C</u>	<u>ClogP$>$1.0</u>
ethyl aceto acetate	No	--	No
cis-3-hexenyl acetate	No	--	Yes
amyl acetate	--	Yes	Yes
hexyl formate	--	--	Yes
diethylene glycol ethyl ether	--	--	No
beta gamma hexenol	No	--	Yes
prenyl acetate	No	--	--
dipropylene glycol	--	Yes	No
ethyl amyl ketone	No	Yes	Yes
methyl hexyl ketone	No	Yes	Yes
methyl n-amyl ketone	No	Yes	Yes
methyl heptene carbonate	Yes	Yes	Yes
methyl heptyl ketone	No	--	Yes
dimethyl octanol	No	--	Yes

hexyl tiglate	No	--	Yes
undecylenic aldehyde	Yes	--	Yes
citral	No	--	Yes
citronellyl acetate	No	--	Yes
undecalactone gamma	Yes	--	Yes
citronellyl nitrile	No	--	Yes
geranyl formate	--		Yes
hydroxycitronellal	No		Yes
phenyl ethyl alcohol	No	Yes	Yes
benzyl alcohol	No	Yes	Yes
methyl nonyl acetaldehyde	No	--	Yes
citronellol	No	--	Yes
benzyl formate	--	--	Yes
methyl chavicol	No	--	Yes
dihydro myrcenol	No	Yes	Yes
heliotropin	Yes	Yes	Yes
methyl octyl acetaldehyde	No	--	Yes
linalool	Yes	Yes	Yes
geranyl nitrile	No	--	Yes
tetra hydro linalool	No	Yes	Yes
jasmone, cis	No	--	Yes
methyl dihydro jasmonate	No	--	Yes
phenoxy ethanol	No	Yes	Yes
dodecalactone gamma	Yes	--	Yes
cyclal c	Yes	--	Yes
ligustral	--	Yes	Yes
para cymene	--	--	Yes
benzyl propionate	--	--	Yes
phenyl acetaldehyde dimethyl acetal	No	--	--
cinnamyl formate	--	--	Yes
geraniol	No	Yes	Yes
phenoxy ethyl propionate	--	--	Yes
methyl benzoate	--	Yes	Yes
anisic aldehyde, para	Yes	Yes	Yes
allyl cyclohexane propionate	No	--	Yes
geranyl acetate	No	--	Yes
phenyl ethyl acetate	No	--	Yes

indol	Yes	Yes	Yes
cis-3-hexenyl salicylate	Yes	--	Yes
helional	No	Yes	Yes
para methyl acetophenone	No	--	Yes
camphene	--	Yes	Yes
cinnamic aldehyde	--	Yes	Yes
dimethyl anthranilate	No	Yes	Yes
vanillin	Yes	--	Yes
methyl isobutenyl tetrahydropyran	Yes	Yes	Yes
limonene	No	Yes	Yes
amyl salicylate	No	--	Yes
benzyl acetate	No	Yes	Yes
benzaldehyde	No	Yes	Yes
para hydroxy phenyl butanone	Yes	--	--
abierate cn	No	Yes	Yes
para cresyl methyl ether	--	Yes	Yes
phenoxy ethyl iso butyrate	--	--	Yes
cymal	Yes	Yes	Yes
carvone laevo	--	Yes	Yes
linalyl acetate	No	Yes	Yes
ethyl vanillin	Yes	Yes	Yes
benzyl acetone	Yes	--	Yes
hexyl cinnamic aldehyde	No	--	Yes
methyl phenyl carbonyl acetate	No	--	Yes
coumarin	Yes	--	Yes
amyl cinnamic aldehyde	No	--	Yes
ionone alpha	Yes	--	Yes
hexyl salicylate (n-)	No	--	Yes
ethyl methyl phenyl glycidate	Yes	Yes	Yes
p.t. buccinal	Yes	--	Yes
eucalyptol	No	Yes	Yes
patchon	No	--	--
methyl cyclo geraniat	--	--	--
linalool oxide	No	--	Yes
terpinolene	--	Yes	Yes
methyl eugenol	No	--	--
alpha terpineol	--	Yes	Yes

eugenol	Y s	Yes	Yes
phenyl ethyl phenyl acetate	No	--	Yes
methyl anthranilate	Yes	Yes	Yes
terpineol	--	--	Yes
ionone-ab	--	--	Yes
triethyl citrate	--	Yes	Yes
iso eugenol	Yes	--	Yes
verdol	No	--	--
beta naphthol methyl ether	Yes	--	--
diethyl phthalate	--	Yes	Yes
beta pinene	No	--	Yes
phenyl ethyl benzoate	No	--	--
benzyl benzoate	--	Yes	Yes
herbavert	Yes	Yes	--
alpha pinene	No	Yes	Yes
ionone gamma methyl	--	--	Yes
diphenyl oxide	No	--	Yes
lyral	Yes	--	Yes
3,5,5-trimethyl hexanal	No	--	--
allyl amyl glycolate	Yes	--	--
anethol	Yes	--	Yes
bacdanol	Yes	--	--
butyl anthranilate	Yes	--	--
calone 1951	Yes	--	--
cantryl 3/041586	No	--	--
cinnamic alcohol	Yes	Yes	Yes
corps 4322	No	--	--
cyclogalbanate 3/024061	Yes	--	--
cyclohexyl anthranilate	No	--	--
cyclopidene	No	--	--
damascenone	Yes	--	Yes
damascone alpha	No	--	Yes
decenal 4- (Z)	Yes	--	Yes
decyl aldehyde	No	Yes	Yes
dihydro iso jasmonate	Y s	--	Yes
dihydroambrate	No	--	--
dimethyl benzyl carbinol	No	--	Yes

dimyrcetol	No	--	--
diphenyl methane	No	Yes	Yes
dulcinyll	No	--	--
ebanol	No	--	--
ethyl-2-methyl butyrate	Yes	--	Yes
floralol	No	--	--
florhydral	No	--	--
freskomenthe/2-sec-butyl	No	--	--
cyclohexanone			
fructose/methyl dioxolan	Yes	--	--
gyrane	No	--	--
hawthanol	No	--	--
hydratropic aldehyde	No	--	Yes
hydroquinone dimethyl ether	No	Yes	--
ionone beta	Yes	--	Yes
iso cyclo citral	Yes	--	--
iso cyclo geraniol	No	--	--
iso hexenyl cyclohexenyl	No	--	Yes
carboxaldehyde / myrac aldehyde			
iso nonyl acetate	--	--	Yes
isopentyrate	No	--	--
keone	Yes	--	Yes
lauric aldehyde	No	--	Yes
livescone	No	--	--
mandarin aldehyde / dodecenal 3-	No	--	--
mayol	No	--	--
methyl nonyl ketone	Yes	--	Yes
methyl salicylate	No	Yes	Yes
myrcene	--	Yes	Yes
nectaryl	No	--	--
nerol	Yes	--	Yes
nerol oxide	No	--	--
nonenal 2-	--	--	Yes
orivone	No	--	--
phenyl acetaldehyde	Yes	Yes	Yes
phenyl hexanol	No	--	Yes
phenyl propyl alcohol	No	--	--

rosalva	No	--	Yes
sandalore	No	--	Yes
tetra hydro myrcenol	No	--	Yes
thymol	No	Yes	Yes
trimenal / 2,5,9-trimethyl dodecadienal	No	--	--
triplal	No	--	Yes
undec-2-en-1-al	No	--	Yes
undecavertol	No	--	--

Zeolites

The term "zeolite" used herein refers to a crystalline aluminosilicate material. The structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure represented by

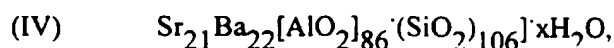
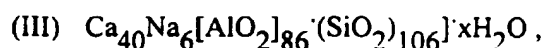
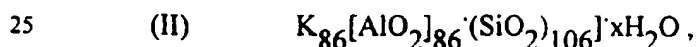
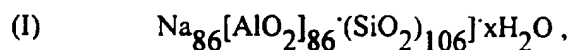


where n is the valence of the cation M, x is the number of water molecules per unit cell, m and y are the total number of tetrahedra per unit cell, and y/m is 1 to 100. Most preferably, y/m is 1 to 5. The cation M can be Group IA and Group IIA elements, such as sodium, potassium, magnesium, and calcium.

The zeolite useful herein is a faujasite-type zeolite, including Type X Zeolite or Type Y Zeolite, both with a nominal pore size of about 8 Angstrom units, typically in the range of from about 7.4 to about 10 Angstrom units.

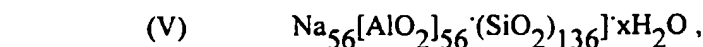
The aluminosilicate zeolite materials useful in the practice of this invention are commercially available. Methods for producing X and Y-type zeolites are well-known and available in standard texts. Preferred synthetic crystalline aluminosilicate materials useful herein are available under the designation Type X or Type Y.

For purposes of illustration and not by way of limitation, in a preferred embodiment, the crystalline aluminosilicate material is Type X and is selected from the following:

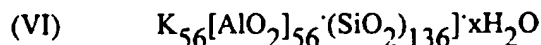


and mixtures thereof, wherein x is from about 0 to about 276. Zeolites of Formula (I) and (II) have a nominal pore size or opening of 8.4 Angstroms units. Zeolites of Formula (III) and (IV) have a nominal pore size or opening of 8.0 Angstroms units.

In another preferred embodiment, the crystalline aluminosilicate material is Type Y and is selected from the following:



10



and mixture thereof, wherein x is from about 0 to about 276. Zeolites of Formula (V) and (VI) have a nominal pore size or opening of 8.0 Angstroms units.

Zeolites used in the present invention are in particle form having an average particle size from about 0.5 microns to about 120 microns, preferably from about 0.5 microns to about 30 microns, as measured by standard particle size analysis technique.

The size of the zeolite particles allows them to be entrained in the fabrics with which they come in contact. Once established on the fabric surface (with their coating matrix having been totally or partially washed away during the laundry process), the zeolites can begin to release their incorporated laundry agents, especially when subjected to heat or humid conditions.

Incorporation of Perfume in Zeolite - The Type X or Type Y Zeolites to be used herein preferably contain less than about 10% desorbable water, more preferably less than about 8% desorbable water, and most preferably less than about 5% desorbable water. Such materials may be obtained by first activating/dehydrating by heating to about 150-350°C, optionally with reduced pressure (from about 0.001 to about 20 Torr), for at least 12 hours. After activation, the agent is slowly and thoroughly mixed with the activated zeolite and, optionally, heated to about 60°C for up to about 2 hours to accelerate absorption equilibrium within the zeolite particles. The perfume/zeolite mixture is then cooled to room temperature and is in the form of a free-flowing powder.

The amount of laundry agent incorporated into the zeolite carrier is less than about 20%, typically less than about 18.5%, by weight of the loaded particle, given the limits on the pore volume of the zeolite. It is to be recognized, however, that the present invention particles may exceed this level of laundry agent by

weight of the particle, but recognizing that excess levels of laundry agents will not be incorporated into the zeolite, even if only deliverable agents are used. Therefore, the present invention particles may comprise more than 20% by weight of laundry agents, by weight of the present invention particles. Since any excess
5 laundry agents (as well as any non-deliverable agents present) are not incorporated into the zeolite pores, these materials are likely to be immediately released to the wash solution upon contact with the aqueous wash medium.

Matrix

Preferred compositions herein further comprise a coating matrix as
10 described in WO 94/28107, published December 8, 1994. The matrix employed in the perfume delivery system of this invention therefore preferably comprises a fluid diol or polyol, such as glycerol, ethylene glycol, or diglycerol (suitable fluid diols and polyols typically have a M.P. below about -10°C) and, optionally but preferably, a solid polyol containing more than three hydroxyl moieties, such as
15 glucose, sorbitol, and other sugars. The solid polyol should be dissolvable with heating in the fluid diol or polyol to form a viscous (approximately 4000 cPs), fluid matrix (i.e., the consistency of honey). The matrix, which is insoluble with the perfume, is thoroughly mixed with the perfumed zeolite and, thereby, entraps and "protects" the perfume in the zeolite. Solubility of the matrix in water enables
20 the perfumed zeolite to be released in the aqueous bath during laundering.

The preferred properties of the matrix formed by the fluid diol or polyol and the solid polyol include strong hydrogen- bonding which enables the matrix to attach to the zeolite at the siloxide sites and to compete with water for access to the zeolite; incompatibility of the matrix with the perfume which enables the
25 matrix to contain the perfume molecules inside the zeolite cage and to inhibit diffusion of the perfume out through the matrix during dry storage; hydrophilicity of the matrix to enable the matrix materials to dissolve in water for subsequent perfume release from the zeolites; and humectancy which enables the matrix to serve as a limited water sink to further protect the perfumed zeolite from humidity
30 during storage.

The matrix material comprises from about 20% to about 100%, preferably from about 50% to about 70%, by weight of the fluid diol or polyol and from 0% to about 80%, preferably from about 30% to about 50%, by weight, of one or more solid polyols. Of course, the proportions can vary, depending on the
35 particular solid polyols and fluid polyols that are chosen. The perfume delivery system comprises from about 10% to about 90%, preferably from about 20% to

about 40%, by weight of the diol/polyol matrix material, the balance comprising the perfume-plus-zeolite.

The present invention may also utilize a glassy particle delivery system comprising the zeolite particle of the present invention. The glass is derived from one or more at least partially water-soluble hydroxylic compounds, wherein at least one of said hydroxylic compounds has an anhydrous, nonplasticized, glass transition temperature, T_g , of about 0°C or higher. Further the glassy particle has a hygroscopicity value of less than about 80%.

The at least partially water soluble hydroxylic compounds useful herein are preferably selected from the following classes of materials.

1. Carbohydrates, which can be any or mixture of: i) Simple sugars (or monosaccharides); ii) Oligosaccharides (defined as carbohydrate chains consisting of 2-10 monosaccharide molecules); iii) Polysaccharides (defined as carbohydrate chains consisting of at least 35 monosaccharide molecules); and iv) Starches.

Both linear and branched carbohydrate chains may be used. In addition chemically modified starches and poly-/oligo-saccharides may be used. Typical modifications include the addition of hydrophobic moieties of the form of alkyl, aryl, etc. identical to those found in surfactants to impart some surface activity to these compounds.

2. All natural or synthetic gums such as alginate esters, carrageenin, agar-agar, pectic acid, and natural gums such as gum arabic, gum tragacanth and gum karaya.

3. Chitin and chitosan.
4. Cellulose and cellulose derivatives. Examples include: i) Cellulose acetate and Cellulose acetate phthalate (CAP); ii) Hydroxypropyl Methyl Cellulose (HPMC); iii) Carboxymethylcellulose (CMC); iv) all enteric/aquateric coatings and mixtures thereof.

5. Silicates, Phosphates and Borates.
6. Polyvinyl alcohol (PVA).
7. Polyethylene glycol (PEG).

Materials within these classes which are not at least partially water soluble and which have glass transition temperatures, T_g , below the lower limit herein of about 0°C are useful herein only when mixed in such amounts with the hydroxylic compounds useful herein having the required higher T_g such that the glassy particle produced has the required hygroscopicity value of less than about 80%.

Glass transition temperature, commonly abbreviated "Tg", is a well known and readily determined property for glassy materials. This transition is described as being equivalent to the liquification, upon heating through the Tg region, of a material in the glassy state to one in the liquid state. It is not a phase transition such as melting, vaporization, or sublimation. [See William P. Brennan, "What is a Tg?" A review of the scanning calorimetry of the glass transition", Thermal Analysis Application Study #7, Perkin-Elmer Corporation, March 1973.] Measurement of Tg is readily obtained by using a Differential Scanning Calorimeter.

For purposes of the present invention, the Tg of the hydroxylic compounds is obtained for the anhydrous compound not containing any plasticizer (which will impact the measured Tg value of the hydroxylic compound). Glass transition temperature is also described in detail in P. Peyser, "Glass Transition Temperatures of Polymers", Polymer Handbook, Third Edition, J. Brandrup and E. H. Immergut (Wiley-Interscience; 1989), pp. VI/209 - VI/277.

At least one of the hydroxylic compounds useful in the present invention glassy particles must have an anhydrous, nonplasticized Tg of at least 0°C, and for particles not having a moisture barrier coating, at least about 20°C, preferably at least about 40 C, more preferably at least 60 C, and most preferably at least about 100 C. It is also preferred that these compounds be low temperature processable, preferably within the range of from about 50 C to about 200 C, and more preferably within the range of from about 60 C to about 160 C. Preferred such hydroxylic compounds include sucrose, glucose, lactose, and maltodextrin.

The "hygroscopicity value", as used herein, means the level of moisture uptake by the glassy particles, as measured by the percent increase in weight of the particles under the following test method. The hygroscopicity value required for the present invention glassy particles is determined by placing 2 grams of particles (approximately 500 micron size particles; not having any moisture barrier coating) in an open container petrie dish under conditions of 90°F and 80% relative humidity for a period of 4 weeks. The percent increase in weight of the particles at the end of this time is the particles hygroscopicity value as used herein. Preferred particles have hygroscopicity value of less than about 50%, more preferably less than about 10%.

The glassy particles useful in the present invention typically comprise from about 10% to about 99.99% of at least partially water soluble hydroxylic compounds, preferably from about 20% to about 90%, and more preferably from about 20% to about 75%. The glassy particles of the present invention also

typically comprise from about 0.01% to about 90% of the present invention particles, preferably from about 10% to about 80%, and more preferably from about 25% to about 80%.

5 Methods for making these glassy particles are extrapolated from the candy-making art. Such methods include, for example, the methods described in U.S. Patent 2,809,895, issued October 15, 1957 to Swisher.

10 In addition to its function of containing/protecting the perfume in the zeolite particles, the matrix material also conveniently serves to agglomerate multiple perfumed zeolite particles into agglomerates having an overall aggregate size in the range of 200 to 1000 microns, preferably 400 to 600 microns. This reduces dustiness. Moreover, it lessens the tendency of the smaller, individual perfumed zeolites to sift to the bottom of containers filled with granular detergents, which, themselves, typically have particle sizes in the range of 200 to 1000 microns.

15 The following nonlimiting example describes a typical laboratory preparation of the perfume delivery composition.

EXAMPLE I

Production of Coated Perfume Carrier Particle

Step 1 Perfume Component Addition to Zeolite:

20 About 1500g. of Zeolite 13X powder is added to a 5L Littleford plough mixer with a jacket temperature of ~140°F. 300g. of perfume components are charged into a pressure bomb and pressurized to 5 psig. These perfume components are:

<u>Components</u>	<u>Wt. Percent</u>
allyl amyl glycolate	0.2
damascenone	0.31
decyl aldehyde	0.51
dihydro iso jasmonate	15.27
helional	1.02
ionone gamma methyl	14.97
linalool	20.37
myrcene	1.02
p.t. buccinal	15.27
para methyl acetophenone	0.51
phenyl ethyl alcohol	20.37
undecavertol	10.18

With the mixer on, the perfume is added to the Littleford and mixed for ~1.75 hours. Cooling water is then added to the jacket for ~15 minutes while mixing continues to complete the perfume loading.

- 5 Step 2 Preparation of glucose/glycerol coating mixture:
About 475g. of glycerol is placed in a 2000 ml beaker and heated on a hot
plate while stirring. About 525g. of glucose is then added to the beaker.
Stirring/heating continues until the temperature of the mixture reads 120°
C. Continue heating and stirring until mixture is clear. Allow to cool to
10 75°F.
- Step 3 Addition of glucose/glycerol coating mixture to Perfume/Zeolite particle:
About 300g of Perfume/Zeolite particles are placed in a Braun food
processor. With processor on, about 125g. of glucose/glycerol mixture is
15 added with a syringe. Continue mixing for eight minutes. Remove from
processor and store in a glass jar under nitrogen.

The laundry particle compositions are used in compositions with deterative ingredients, as follows.

Optional Deterative Adjuncts

- As a preferred embodiment, the conventional detergent ingredients employed herein can be selected from typical detergent composition components such as deterative surfactants and deterative builders. Optionally, the detergent ingredients can include one or more other deterative adjuncts or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual deterative adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. Such adjuncts which can be included in detergent compositions employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 80% of the detergent ingredients, preferably from about 0.5% to about 20%), include color speckles, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, solvents, solubilizing agents, chelating agents, clay soil removal/anti-redeposition agents, polymeric dispersing agents, processing aids, fabric softening components, static control agents, bleaching agents, bleaching activators, bleach stabilizers, etc.

Deterstive Surfactant - Deterstive surfactants included in the fully-formulated detergent compositions afforded by the present invention comprises at least 1%, preferably from about 1% to about 99.8%, by weight of detergent composition depending upon the particular surfactants used and the effects desired. In a highly preferred embodiment, the deterstive surfactant comprises from about 5% to about 80% by weight of the composition.

The deterstive surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Preferred detergent compositions comprise anionic deterstive surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants.

Nonlimiting examples of surfactants useful herein include the conventional $C_{11}-C_{18}$ alkyl benzene sulfonates and primary, secondary and random alkyl sulfates, the $C_{10}-C_{18}$ alkyl alkoxy sulfates, the $C_{10}-C_{18}$ alkyl polyglycosides and their corresponding sulfated polyglycosides, $C_{12}-C_{18}$ alpha-sulfonated fatty acid esters, $C_{12}-C_{18}$ alkyl and alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), $C_{12}-C_{18}$ betaines and sulfobetaines ("sultaines"), $C_{10}-C_{18}$ amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

One class of nonionic surfactant particularly useful in detergent compositions of the present invention is condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range of from 5 to 17, preferably from 6 to 14, more preferably from 7 to 12. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C_9-C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the $C_{14}-C_{15}$ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol, the $C_{12}-C_{15}$ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol, and mixtures thereof.

Another suitable class of nonionic surfactants comprises the polyhydroxy fatty acid amides of the formula:



wherein: R^1 is H , C_1-C_8 hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most

preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{32} hydrocarbyl moiety, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{19} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)_n-CH_2OH$, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or polysaccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R^1 is preferably methyl or hydroxyalkyl. If lower sudsing is desired, R^1 is preferably C_2 - C_8 alkyl, especially n-propyl, iso-propyl, n-butyl, isobutyl, pentyl, hexyl and 2-ethyl hexyl.

$R^2-CO-N<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc. (It is to be understood that separate portions of the polyhydroxy fatty acid amides can be used both as the deterative surfactant in the detergent compositions herein, and as the solid polyol of the matrix material used to coat the preferred zeolites.)

Enzymes - Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In

this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry detergent composition.

- 5 Preferred detergent enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases.

- Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term
10 "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the
15 compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may also be desirable in highly concentrated detergent formulations.

- 20 Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous
25 enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH
30 protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available
35 as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Amylases suitable herein include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to

the hereinbefore incorporated WO 9402597. Novo. Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano."

or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex
5 *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

10 Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash
15 to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic
20 detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al. July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such
25 formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful
30 *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Enzyme Stabilizing System - Enzyme-containing herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The
35 enzyme stabilizing system can be any stabilizing system which is compatible with the deterative enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a

manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to

react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

Bleaching Compounds - Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other

cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable
 5 examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxododecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S.
 10 Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

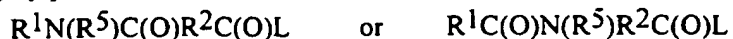
15 Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

20 A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with
 25 silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in
 30 aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See
 35 also U.S. 4,634,551 for other typical bleaches and activators useful herein.

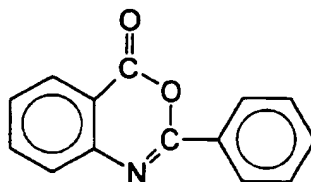
Highly preferred amido-derived bleach activators are those of the formulae:



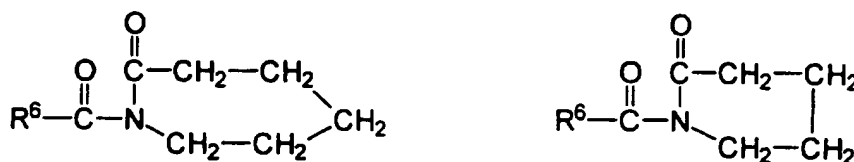
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or

aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

5 If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of
10 these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_3(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based
15 bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and
20 processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Builders - Detergent builders can optionally be included in the compositions
25 herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will
30 typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be
35 excluded.

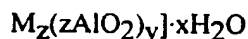
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates

(exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function
 5 surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as
 10 the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by
 15 methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from
 20 Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

25 Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

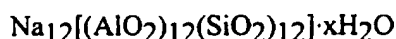
Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular
 30 detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range
 35 from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be

naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their

biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the
5 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-
10 dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued
15 March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should
20 be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such
25 as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Polymeric Soil Release Agent - Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent
30 compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic
35 segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the

hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic species, see U.S. 4,956,447, issued September 11, 1990 to Gosselink, et al., as well as
5 noncharged monomer units, and their structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

10 Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely
15 crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451,
20 November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped
25 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988
30 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate
35 esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an

example being an ester composition made from m-sulfo benzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 80-90% by weight of polyoxyethylene terephthalate derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

Another preferred SRA is an oligomer having empirical formula (CAP)₂(EG/PG)₅(T)₅(SIP)₁ which comprises terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units and which is preferably terminated with end-caps (CAP), preferably modified isethionates, as in an oligomer comprising one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a defined ratio, preferably about 0.5:1 to about 10:1, and two end-cap units derived from sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said SRA preferably further comprises from 0.5% to 20%, by weight of the oligomer, of a crystallinity-reducing stabiliser, for example an anionic surfactant such as linear sodium dodecylbenzenesulfonate or a member selected from xylene-, cumene-, and toluene- sulfonates or mixtures thereof. these stabilizers or modifiers being introduced into the synthesis vessel, all as taught in

U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na-2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl-5-sulfoisophthalate, EG and PG.

Yet another group of preferred SRA's are oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred are esters of the empirical formula:



wherein CAP, EG/PG, PEG, T and SIP are as defined hereinabove, (DEG) represents di(oxyethylene)oxy units, (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units, (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, x is from about 1 to about 12, y' is from about 0.5 to about 25, y'' is from 0 to about 12, y''' is from 0 to about 10, y'+y''+y''' totals from about 0.5 to about 25, z is from about 1.5 to about 25, z' is from 0 to about 12; z + z' totals from about 1.5 to about 25, q is from about 0.05 to about 12; m is from about 0.01 to about 10, and x, y', y'', y''', z, z', q and m represent the average number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from about 500 to about 5,000.

Preferred SEG and CAP monomers for the above esters include Na-2-(2,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2-hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred SRA esters in this class include the product of transesterifying and oligomerizing sodium 2-{2-(2-hydroxyethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)ethoxy}-ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)₂(T)₅(EG/PG)_{1.4}(SEG)_{2.5}(B)_{0.13} wherein CAP is (Na+O₃S[CH₂-CH₂O]_{3.5})- and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF, made by grafting acrylic monomers onto sulfonated polyesters. These SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie. Still other classes include: (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate onto proteins such as caseins, see EP 457,205 A to BASF (1991); and (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al., DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989 and 4,525,524.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to
5 not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

10 A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if
15 utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent
20 compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in
25 U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application
30 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent
35 includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble

acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the
5 maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil
10 removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as
15 polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into
20 subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John
25 Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include:
30 Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the amino-coumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-
35 bis(benzoxazol-2-yl)thiophene; 2-styryl-naphtho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein
5 the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which
10 relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent
15 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to
20 about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- 25 (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene
30 glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about
35 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone

compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

10 The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight
15 %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight
20 ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like
25 PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred
30 alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing
35 machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of

the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts

such as $MgCl_2$, $MgSO_4$, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

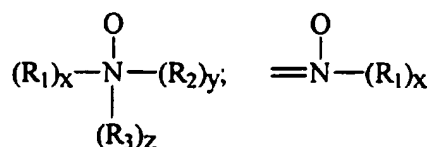
The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye

transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000:

more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

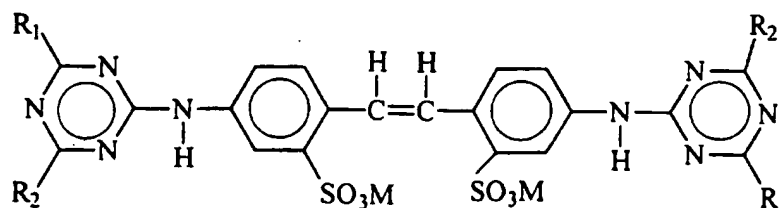
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

5 When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the
10 preferred hydrophilic optical brightener useful in the detergent compositions herein.

 When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed
15 under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

 When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy
20 Corporation.

 The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g.,
25 PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for
30 fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with
35 relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

5 High Density Granular Detergent Composition

The perfume delivery composition can be used in both low density (below 550 grams/liter) and high density granular detergent compositions in which the density of the granule is at least 550 grams/liter. Such high density detergent compositions typically comprise from about 30% to about 90% of deterative
10 surfactant.

Low density compositions can be prepared by standard spray- drying processes. Various means and equipment are available to prepare high density granular detergent compositions. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which
15 often have a density less than about 500 g/l. Accordingly, if spray drying is used as part of the overall process, the resulting spray-dried detergent particles must be further densified using the means and equipment described hereinafter. In the alternative, the formulator can eliminate spray-drying by using mixing, densifying and granulating equipment that is commercially available. The following is a
20 nonlimiting description of such equipment suitable for use herein.

High speed mixer/densifiers can be used in the present process. For example, the device marketed under the trademark "Lodige CB30" Recycler comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. Other such apparatus includes the devices
25 marketed under the trademark "Shugi Granulator" and under the trademark "Drais K-TTP 80". Equipment such as that marketed under the trademark "Lodige KM600 Mixer" can be used for further densification.

In one mode of operation, the compositions are prepared and densified by passage through two mixer and densifier machines operating in sequence. Thus,
30 the desired compositional ingredients can be admixed and passed through a Lodige mixture using residence times of 0.1 to 1.0 minute then passed through a second Lodige mixer using residence times of 1 minute to 5 minutes.

In another mode, an aqueous slurry comprising the desired formulation ingredients is sprayed into a fluidized bed of particulate surfactants. The resulting
35 particles can be further densified by passage through a Lodige apparatus, as noted above. The perfume delivery particles are admixed with the detergent composition in the Lodige apparatus.

The final density of the particles herein can be measured by a variety of simple techniques, which typically involve dispensing a quantity of the granular detergent into a container of known volume, measuring the weight of detergent and reporting the density in grams/liter.

- 5 Once the low or high density granular detergent "base" composition is prepared, the agglomerated perfume delivery system of this invention is added thereto by any suitable dry-mixing operation.

Deposition of Perfume onto Fabric Surfaces

- 10 The method of washing fabrics and depositing perfume thereto comprises contacting said fabrics with an aqueous wash liquor comprising at least about 100 ppm of conventional deterative ingredients described hereinabove, as well as at least about 0.1 ppm of the above-disclosed perfume delivery system. Preferably, said aqueous liquor comprises from about 500 ppm to about 20,000 ppm of the conventional deterative ingredients and from about 10 ppm to about 200 ppm of the
15 perfume delivery system.

- The perfume delivery system works under all circumstances, but is particularly useful for providing odor benefits on fabrics during storage, drying or ironing. The method comprises contacting fabrics with an aqueous liquor containing at least about 100 ppm of conventional deterative ingredients and at
20 least about 1 ppm of the perfume delivery composition such that the perfumed zeolite particles are entrained on the fabrics, storing line-dried fabrics under ambient conditions with humidity of at least 20%, drying the fabric in a conventional automatic dryer, or applying heat to fabrics which have been line-dried or machine dried at low heat (less than about 50°C) by conventional
25 ironing means (preferably with steam or pre-wetting).

 The following nonlimiting examples illustrate the parameters of and compositions employed within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

Examples II - IV

- 30 Several detergent compositions made in accordance with the invention and specifically for top-loading washing machines are exemplified below incorporating the perfume particle prepared in Example I.

<u>Base Granule</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Aluminosilicate	18.0	22.0	24.0
Sodium Sulfate	10.0	19.0	6.0

Sodium Polyacrylate Polymer	3.0	2.0	4.0
PolyethyleneGlycol (MW=400)	2.0	1.0	--
C12-13 Linear Alkylbenzene	6.0	7.0	8.0
Sulfonate, Na			
C14-16 Secondary Alkyl Sulfate, Na	3.0	3.0	--
C14-15 Alkyl Ethoxylated Sulfate, Na	3.0	9.0	--
Sodium Silicate	1.0	2.0	3.0
Brightener 24/476	0.3	0.3	0.3
Sodium Carbonate	7.0	26.0	
Carboxymethyl Cellulose	--	--	1.0
DTPMPA ⁷	--	--	0.5
DTPA ¹	0.5	--	--
<u>Admixed Agglomerates</u>			
C14-15 Alkyl Sulfate, Na	5.0	--	--
C12-13 Linear Alkylbenzene	2.0	--	--
Sulfonate, Na			
Sodium Carbonate	4.0	--	--
Polyethylene Glycol (MW=4000)	1.0	--	--
<u>Admix</u>			
Sodium Carbonate	--	--	13.0
C12-15 Alkyl Ethoxylate (EO=7)	2.0	0.5	2.0
C12-15 Alkyl Ethoxylate (EO=3)	--	--	2.0
Perfume Spray-On	0.3	1.0	0.3
Perfume Particles ⁹	2.0	2.0	2.0
Polyvinylpyrrolidone	0.5	--	--
Polyvinylpyridine N-oxide	0.5	--	--
Polyvinylpyrrolidone-	0.5	--	--
polyvinylimidazole			
Distearylamine & Cumene Sulfonic	2.0	--	--
Acid			
Soil Release Polymer ²	0.5	--	--
Lipolase Lipase (100.000 LU/l) ⁴	0.5	--	0.5
Termamyl Amylase (60 KNU/g) ⁴	0.3	--	0.3
CAREZYME® Cellulase (1000	0.3	--	--
CEVU/g) ⁴			
Protease (40mg/g) ⁵	0.5	0.5	0.5
NOBS ³	5.0	--	--

TAED ⁸	--	--	3.0
Sodium Percarbonate	12.0	--	--
Sodium Perborate Monohydrate	--	--	22.0
Polydimethylsiloxane	0.3	--	3.0
Sodium Sulfate	--	--	3.0
Miscellaneous (water, etc.)	<u>balance</u>	<u>balance</u>	<u>balance</u>
Total	100	100	100

1. Diethylene Triamine Pentaacetic Acid
2. Made according to U.S. Patent 5,415,807, issued May 16, 1995 to Gosselink et al
3. Nonanoyloxybenzenesulfonate
- 5 4. Purchased from Novo Nordisk A/S
5. Purchased from Genencor
6. Purchased from Ciba-Geigy
7. Diethylene Triamine Pentamethylene Phosphonic Acid
8. Tetra Acetyle Ethylene Diamine
- 10 9. From Example I

Examples V-XVI

- The following detergent compositions containing a perfume particle from Example I accordance with the invention are especially suitable for front loading washing machines. The compositions are made in the manner of Examples II-IV.

	<u>(% Weight)</u>	
<u>Base Granule</u>	<u>V</u>	<u>VI</u>
Aluminosilicate	15.0	--
Sodium Sulfate	2.0	--
C12-13 Linear Alkylbenzene Sulfonate, Na	3.0	--
DTPMPA ¹	0.5	--
Carboxymethylcellulose	0.5	--
Acrylic Acid/Maleic Acid Co-polymer	4.0	--
<u>Admixed Agglomerates</u>		
C14-15 Alkyl Sulfate, Na	--	11.0
C12-13 Linear Alkylbenzene Sulfonate, Na	5.0	--
C18-22 Alkyl Sulfate, Na	2.0	--

56

Sodium Silicate	4.0	--
Aluminosilicate	12.0	13.0
Carboxymethylcellulose	--	0.5
Acrylic Acid/Maleic Acid Co-polymer	--	2.0
Sodium Carbonate	8.0	7.0
<u>Admix</u>		
Perfume Spray-On	0.3	0.5
Perfume Particles ⁴		
C12-15 Alkyl Ethoxylate (EO=7)	4.0	4.0
C12-15 Alkyl Ethoxylate (EO=3)	2.0	2.0
Acrylic Acid/Maleic Acid Co-polymer	--	3.0
Crystalline Layered Silicate ²	--	12.0
Sodium Citrate	5.0	8.0
Sodium Bicarbonate	5.0	5.0
Sodium Carbonate	6.0	15.0
Polyvinylpyrrolidone	0.5	0.5
Alcalase protease ³ (3.0 AU/g)	0.5	1.0
Lipolase Lipase ³ (100,000 LU/1)	0.5	0.5
Termamyl Amylase ³ (60KNU/g)	0.5	0.5
CAREZYME® Cellulase ³ (1000CEVU/g)	0.5	0.5
Sodium Sulfate	4.0	0.0
Miscellaneous (water, etc.)	<u>balance</u>	<u>balance</u>
Total	100.0	100.0

1. Diethylene Triamine Pentamethylenephosphonic Acid

2. SKS 6 commercially available from Hoechst

3. Purchased from Novo Nordisk A/S

4. From Example I

5

	<u>(% Weight)</u>	
<u>Base Granules</u>	<u>VII</u>	<u>VIII</u>
Aluminosilicate	15.0	15.0
Sodium Sulfate	2.0	0.0
C12-13 Linear Alkylbenzene Sulfonate.	3.0	3.0
Na		
Cationic Surfactant ¹	1.0	1.0
DTPMPA ²	0.5	0.5

Carboxymethylcellulose	0.5	0.5
Acrylic Acid/Maleic Acid Co-polymer	3.0	2.0
<u>Admixed Agglomerates</u>		
C12-13 Linear Alkylbenzene Sulfonate, Na	5.0	5.0
C18-22 Alkyl Sulfate, Na	2.0	2.0
Sodium Silicate	3.0	4.0
Aluminosilicate	8.0	8.0
Sodium Carbonate	8.0	4.0
<u>Admix</u>		
Perfume Spray-On	0.3	0.3
Perfume Particles ⁵	2.0	2.0
C12-15 Alkyl Ethoxylate (EO=7)	2.0	2.0
C12-15 Alkyl Ethoxylate (EO=3)	1.0	1.0
Sodium Citrate	2.0	2.0
Sodium Bicarbonate	1.0	--
Sodium Carbonate	11.0	10.0
TAED ³	4.0	5.0
Sodium Perborate	10.0	10.0
Polyethylene Oxide	--	0.3
Bentonite	--	10.0
Savinase Protease (4.0 KNPU/g) ⁴	1.0	1.0
Lipolase Lipase (100.000 LU/g) ⁴	0.5	0.5
Termamyl Amylase (60KNU/g) ⁴	0.5	0.5
CAREZYM® Cellulase (1000CEVU/g) ⁴	0.5	0.5
Sodium Sulfate	1.0	--
Miscellaneous (water, etc.)	<u>balance</u>	<u>balance</u>
Total	100.0	100.0

1. C12-14 Dimethyl Hydroxyethyl Quaternary Ammonium Compound
2. Diethylene Triamine Pentamethylenephosphonic Acid
3. Tetra Acetyl Ethylene Diamine
- 5 4. Purchased from Novo Nordisk A/S
5. From Example I

% Weight**IX**

Agglomerate

C12-13 Linear Alkylbenzene Sulfonate, Na	5.0
C14-16 Secondary Alkyl Sulfate, Na	3.0
C14-15 Alkyl Sulfate, Na	9.0
Aluminosilicate	10.0
Sodium Carbonate	6.0
Acrylic/Maleic Co-polymer	3.0
Carboxymethylcellulose	0.5
DTPMPA ¹	0.5

% Weight**Admix****IX**

C12-15 Alkyl Ethoxylate (EO=5)	5.0
Perfume Spray-On	0.5
Perfume Particles ⁸	3.0
Crystalline Layered Silicate ²	10.0
HEDP ³	0.5
Sodium Citrate	2.0
TAED ⁴	6.0
Sodium Percarbonate	20.0
Soil Release Polymer ⁵	0.3
Savinase Protease (4 KNPU/g) ⁶	1.5
Lipolase Lipase (100.000LU/g) ⁶	0.5
CAREZYME® Cellulase (1000 CEVU/g) ⁶	0.5
Termamyl Amylase (60KNU/g) ⁶	0.5
Silica/Silicone Suds Suppressor	5.0
Brightener 49 ⁷	0.3
Brightener 47 ⁷	0.3
Miscellaneous (water, etc.)	<u>balance</u>
Total	100.0

1. Diethylene Triamine Pentamethylenephosphonic Acid
2. SKS6 commercially available from Hoeschst
3. Hydroxyethylidene 1,1 Diphosphonic Acid
- 5 4. Tetra acetyl ethylene diamine
5. Made according to U.S. Patent 5,415,807 issued May 16, 1995 to Gosselink et al
6. Purchased from Novo Nordisk A/S
7. Purchased from Ciba-Geigy

8. From Example I

The following detergent compositions according to the invention are suitable for low wash volume, top loading washing machines.

5

	(% Weight)
<u>Base Granules</u>	<u>X</u>
Aluminosilicate	7.0
Sodium Sulfate	3.0
PolyethyleneGlycol (MW=4000)	0.5
Acrylic Acid/Maleic Acid Co-polymer	6.0
Cationic Surfactant ¹	0.5
C14-16 Secondary Alkyl Sulfate, Na	7.0
C12-13 Linear Alkylbenzene Sulfonate, Na	13.0
C14-15 Alkyl Ethoxylated Sulfate, Na	6.0
Crystalline Layered Silicate ²	6.0
Sodium Silicate	2.0
Oleic Fatty Acid, Na	1.0
Brightener 49 ⁷	0.3
Sodium Carbonate	28.0
DTPA ³	0.3
<u>Admix</u>	
C12-15 Alkyl Ethoxylate (EO=7)	1.0
Perfume Spray-On	1.0
Perfume Particles ⁸	2.0
Soil Release Polymer ⁴	0.5
Polyvinylpyrrolidone	0.3
Polyvinylpyridine N-Oxide	0.1
Polyvinylpyrrolidone-polyvinylimidazole	0.1
Lipolase Lipase (100.000LU/g) ⁶	0.3
Termamyl Amylase (60KNU/g) ⁶	0.1
CAREZYME® Cellulase (1000 CEVU/g) ⁶	0.1
Savinase (4.0 KNPU/g) ⁶	1.0
NOBS ⁵	4.0
Sodium Perborate Monohydrate	5.0
Miscellaneous (water, etc.)	<u>balance</u>
T tal	100.0

1. C12-14 Dimethyl Hydroxyethyl Quaternary Ammonium Compound
2. SKS 6 commercially available from Hoechst
3. Diethylene Triamine Pentaacetic Acid
4. Made according to U.S. patent 5,415,807 issued May 16, 1995 to Gosselink et al
- 5 5. Nonanoyloxybenzenesulfonate
6. Purchased from Novo Nordisk A/S
7. Purchased from Ciba-Geigy
8. From Example I

10

Examples XI-XVII

The following detergent compositions according to the invention are suitable for machine and handwashing operations. The base granule is prepared by a conventional spray drying process in which the starting ingredients are formed into a slurry and passed through a spray drying tower having a counter current stream of hot air (200-400 C) resulting in the formation of porous granules. The remaining adjunct detergent ingredients are sprayed on or added dry.

<u>Base Granule</u>	<u>XI</u>	<u>XII</u>	<u>XIII</u>
C12-13 Alkylbenzene Sulfonate, Na	19.0	18.0	19.0
Cationic Surfactant ⁵	0.5	0.5	--
DTPMPA ⁶	0.3	--	--
DTPA ²	--	0.3	--
Sodium Tripolyphosphate	25.0	19.0	29.0
Acrylic/Maleic Co-polymer	1.0	0.6	--
Carboxymethylcellulose	0.3	0.2	0.3
Brightener 49/15/33 ⁴	0.2	0.2	0.2
Sodium Sulfate	28.0	39.0	15.0
Sodium Silicate (2.0R)	7.5	--	--
Sodium Silicate (1.6R)	--	7.5	6.0
<u>Admix</u>			
Sodium Carbonate	5.0	6.0	20.0
C12-13 Alkly Ethoxylate (EO=7)	0.4	--	1.2
Savinase ³ Protease (4KNPY/g)	0.6	--	1.0
Termamyl ³ Amylase (60KNU/g)	0.4	--	--
Lipolase ³ Lipase (100,000 LU/l)	0.1	0.1	0.1
Sav/Ban ³ (6 KNPu/100 KNU/g)	--	0.3	--

CAREZYME® ³ Cellulase (1000 CEVU/g)	--	0.1	--
Soil Release Polymer ¹	0.1	0.1	0.3
Perfume Spray-On	0.4	0.4	0.4
Perfume Particles ⁷	3.0	3.0	3.0
Miscellaneous (water, etc.)	<u>balance</u>	<u>balance</u>	<u>balance</u>
Total	100.0	100.0	100.0

1. Made according to U.S. patent 5,415,807 issued May 16, 1995 to Gosselink et al
2. Diethylene Triamine Pentaacetic Acid
3. Purchased from Novo Nordisk A/S
- 5 4. Purchased from Ciba-Geigy
5. C12-14Dimethyl Hydroxyethyl Quaternary Ammonium Compound
6. Diethylene Triamine Pentamethylenephosphoric Acid
7. From Example I

10

Examples XIV-XVII

<u>Base Granule</u>	<u>XIV</u>	<u>XV</u>	<u>XVI</u>	<u>XVII</u>
C12-13 Alkly Benzene Sulfonate, Na	20.0	18.0	18.0	10.0
C12-16 Alkly Sulfate, Na	--	--	--	15.0
Cationic Surfactant ⁶	0.6	0.6	0.6	--
DTPMPA ⁷	0.8	0.7	--	--
DTPA ²	--	--	0.8	0.8
Sodium Tripolyphosphate	25.0	22.0	19.0	25.0
Acrylic/Maleic Co-polymer	1.0	1.0	0.6	--
Carboxymethyl Cellulose	0.4	0.4	0.2	0.9
Brightener 49/15 ⁴	0.2	0.2	0.1	0.1
Sodium Sulfate	--	21.0	24.0	13.0
Sodium Silicate 2.0 R	6.0	--	7.5	--
Magnesium Sulfate 1.6 R	0.6	0.6	--	--
<u>Admix</u>				
Sodium Carbonate	18.0	13.0	15.0	18.0
C12-13 Alkyl Ethoxylate (EO=7)	--	--	--	1.0
C12-16 Alkyl Acid	--	--	--	1.0
Sodium Perborate Monohydrate	2.7	2.5	2.0	2.3
NOBS ³	2.2	2.0	1.9	2.3

Savinase ⁵ (4 KNPU/g)	0.9	0.8	--	0.2
Termamyl ⁵ Amylase (60 KNU/g)	0.4	0.4	--	0.5
Lipolase ⁵ Lipase (100,000 LU/l)	0.1	0.1	0.1	--
SAV/BAN ⁵ (6 KNPU/100 KNU/g)	--	--	0.4	--
Carezyme Cellulase® ⁵ (1000 CEVU/g)	0.1	0.1	0.1	0.1
Alumino Silicate	--	--	--	8.0
Soil Release Polymer ¹	0.2	0.2	0.1	0.2
Perfume Spray-on	0.4	0.4	0.4	0.4
Perfume Particles ⁸	3.0	3.0	3.0	3.0
Miscellaneous (water, etc)	<u>balance</u>	<u>balance</u>	<u>balance</u>	<u>balance</u>
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

1. Made according to U.S. Patent 5,415,807 issued May 16, 1995 to Gosselink et al
2. Diethylene Trimine Pentaacetic Acid
3. Nonanoyloxybenzenesulfonate
- 5 4. Purchased from Ciba-Geigy
5. Purchased from NOVO Nordisk A/S
6. C12-14 Dimethol Hydroxethyl Quaternary Ammonium Compound
7. Diethylene Triamine Penlamethylenephosphonic Acid
8. From Example I

10

EXAMPLES XVIII - XXIII

The following detergent compositions according to the invention are especially suitable for front loading machines.

	<u>(% Weight)</u>					
	<u>XVIII</u>	<u>XIX</u>	<u>XX</u>	<u>XXI</u>	<u>XXII</u>	<u>XXIII</u>
<u>Base Granule</u>						
C14-15 Alkyl Sulfate, Na	0.8	--	--	--	--	--
Aluminosilicate	13.5	--	--	--	--	--
Brightener 15/24 ¹	0.2	--	--	--	--	--
Magnesium Sulfate	0.4	--	--	--	--	--
Acrylic Acid/Maleic Acid	3.8	--	--	--	--	--
Co-polymer						
DTPMPA ⁸	0.6	--	--	--	--	--
<u>Admixed Agglomerates</u>						
C12-13 linear alkylbenzene sulfonate, Na	--	6.0	2.0	--	--	6.0

C18-22 Alkyl Sulfate, Na	--	2.0	0.6	--	--	2.0
C14-15 Alkyl Sulfate, Na	2.0	2.0	6.0	8.0	12.0	2.0
Aluminosilicate	8.0	6.0	6.0	6.0	6.0	6.0
Sodium Carbonate	6.0	3.5	3.5	3.5	3.5	3.5
C12-15 Alkyl Ethoxylate (EO=3)	0.2	--	--	--	--	--
Carboxymethyl Cellulose	0.4	0.4	0.4	0.4	0.4	0.2
C12-15 Alkyl Ethoxylated Sulfate, Na	6.0	1.0	2.0	2.0	3.0	1.0
C18-22 Alkyl Ethoxylate (EO= 80)	0.2	--	--	--	--	--
Magnesium Sulfate	--	0.2	0.4	0.8	0.8	0.2
<u>Admix</u>						
Soil Release Polymer ²	0.3	--	0.3	0.3	0.3	--
Sodium Perborate - Tetrahydrate	12.0	12.0	--	--	--	--
Sodium Perborate - Monohydrate	9.0	--	--	--	--	--
Sodium Carbonate	9.0	18.0	10.0	5.0	5.0	15.0
Perfume Spray-on	0.4	0.4	0.4	0.4	0.4	0.4
Perfume Particles ⁹	3.0	3.0	3.0	3.0	3.0	3.0
C12-15 Alkyl Ethoxylate (EO=5)	4.0	5.0	5.0	5.0	8.0	2.0
Savinase ³	0.4	0.8	0.8	0.8	0.8	0.8
Protease(4KNPU/g)						
Termamyl ³ Amylase (60KNU/g)	0.7	0.1	0.7	0.7	0.7	0.1
Lipolase Lipase ³ (100,000 LU/g)	0.4	--	0.2	0.2	0.2	--
Carezyme ® ³ Cellulase (1000 CEVU/g)	0.1	--	0.2	0.2	0.2	0.3
TAED ⁶	5.0	3.1	5.0	5.0	5.0	3.1
Starch	0.6	--	0.5	--	--	--
Sodium Citrate	5.0	2.0	3.0	3.0	2.0	1.0
Sodium Silicate 2.0R	3.0	--	1.0	--	--	2.0
Sodium Percarbonate	--	--	18.0	20.0	20.0	9.0
Crystalline Layered Silicate ⁴	--	8.0	8.0	11.0	8.0	5.0

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Polyvinylpyridine N-Oxide	--	--	0.1	0.1	0.1	--
Polyvinylpyrrolidone-	--	--	0.1	0.1	0.1	--
polyvinylimidazole						
Aluminosilicate	--	13.0	11.0	8.0	4.0	12.0
DTPMPA ⁸	--	0.2	0.4	0.8	0.8	--
Acrylic Acid/Maleic Acid	--	1.5	2.5	4.5	4.5	1.5
Copolymer						
HEDP ⁵	--	0.3	0.5	0.5	--	0.3
N-Cocoyl N-Methyl	--	2.0	2.0	2.0	4.0	1.0
Glucamine						
Brightener 15/49 ¹	--	0.2	0.2	0.2	0.2	0.1
Sodium Bicarbonate	--	2.0	--	--	--	--
Sodium Sulfate	0.2	--	6.0	--	--	--
Cationic Surfactant ⁷	--	--	--	--	--	2.0
Glycerol	--	--	--	--	--	0.7
Bentanite	--	--	--	--	--	0.3
Misc.	<u>balance</u>	<u>balance</u>	<u>balance</u>	<u>balance</u>	<u>balance</u>	<u>balance</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0

1. Purchased from CIBA-Geigy
2. Made according to U.S. Patent 5,415,807 issued 5/16/95 to Gosselink Et. Al.
3. Purchased from NOVO Nordisk A/S
- 5 4. SKS6 commercially available from Hoechst
5. Hydroxyethylidene 1, 1 Disphosphonic Acid
6. Tetra Acetyl ethylene diamine
7. C12-14 Dimethyl Hydroxyethyl Quaternary Ammonium Compound
8. Diethylene Triamine Pentamethylenephosphonic Acid
- 10 9. From Example I

Examples XXIV-XXV

The detergent composition is made in accordance with the invention.

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	<u>XXIV</u>	<u>XXV</u>
<u>Base Granule</u>		
C14-15 Alkyl Sulfate, Na	9.0	25.0

C ₁₂₋₁₃ Linear Alkylbenzene Sulfonate, Na	15.0	15.0
C ₁₄₋₁₆ Secondary Alkyl Sulfate, Na	10.0	--
Sodium Polyacrylate Powder	7.0	7.0
Brightener 15/49 ³	0.3	0.3
Polyvinylpyrrolidone	0.1	0.1
Soil Release Polymer	0.4	0.4
<u>Admix</u>		
C ₁₄₋₁₅ Alkyl Ethoxylate (EO=7)	3.0	3.0
Crystalline Layered Silicate ²	9.0	9.0
Aluminosilicate	8.0	8.0
Sodium Carbonate	14.4	14.4
Perfume Spray-On	0.3	0.3
Perfume Particle ⁶	3.0	3.0
Sodium Perborate, Monohydrate	4.0	4.0
NOBS ⁴	4.5	4.5
Crystalline Layered Silicate	3.0	3.0
Termamyl ⁵ Amylase (60 KNU/g)	0.5	0.5
Savinase ⁵ Protease(4KNPU/g)	1.2	1.2
Miscellaneous (water, etc.)	<u>balance</u>	<u>balance</u>
Total	100.0	100.0

1. Made according to U.S. Patent 5, 415, 807 issued 5/16/95 to Gosselink et. al.
2. SKS-6 commercially available from Hoechst
3. Purchased from CIBA - Geigy
- 5 4. Nonanoyloxybenzenesulfonate
5. Purchased from Novo Nordisk A/S
6. From Example I

EXAMPLE XXVI

- 10 The following detergent composition according to the invention is in the form of a laundry bar which is particularly suitable for handwashing operations.

		% Weight
	Coconut Fatty Alkyl Sulfate	30.0
	Sodium Tripolyphosphate	5.0
15	Tetrasodium Pyrophosphate	5.0
	Sodium Carbonate	20.0

		Sodium Sulfate	5.0
		Calcium Carbonate	5.0
		$\text{Na}_{1.9}\text{K}_{0.1}\text{Ca}(\text{CO}_3)_2$	15.0
		Aluminosilicate	2.0
5		Coconut Fatty Alcohol	2.0
		Perfume Particle ¹	2.0
		Perfume Spray-On	1.0
		Miscellaneous (water, etc.)	<u>Balance</u>
		Total	100.0
10	1.	From Example 1.	

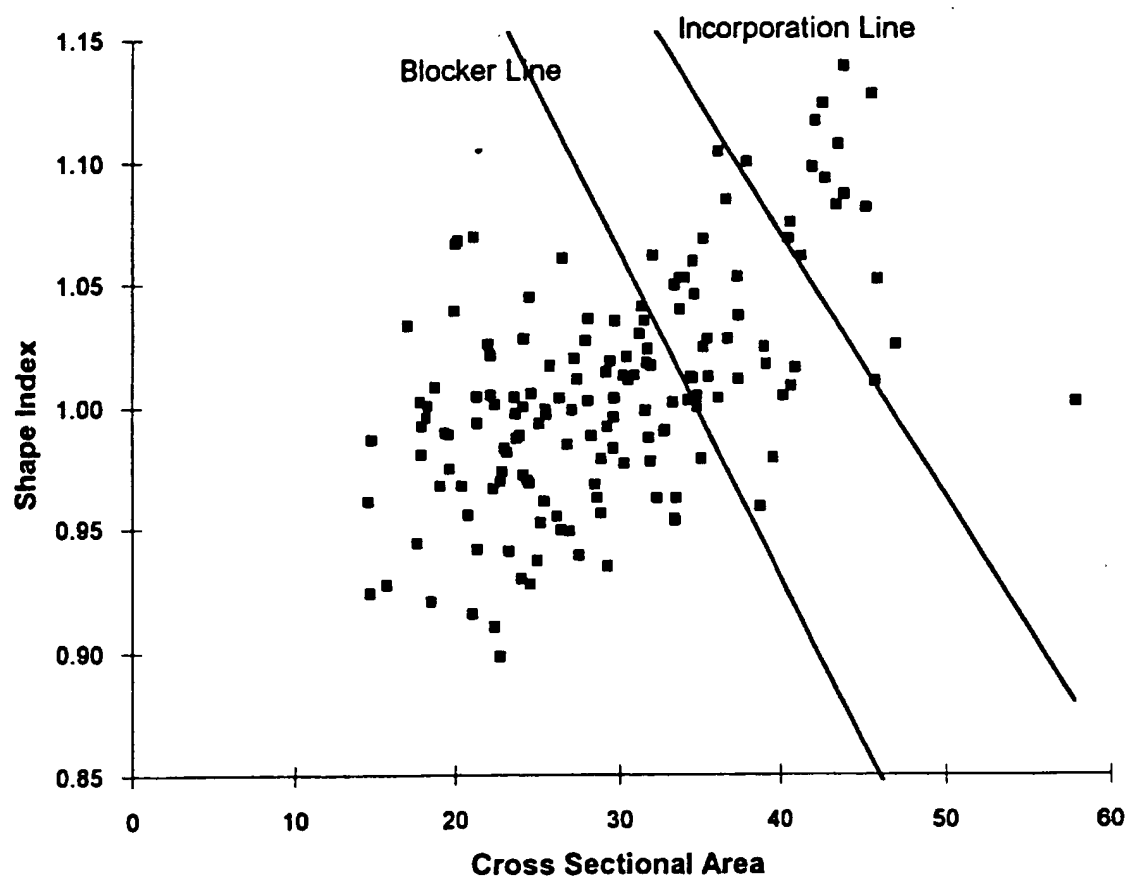
WHAT IS CLAIMED IS:

1. A laundry particle comprising:
 - a) a porous carrier selected from the group consisting of Zeolite X, Zeolite Y, and mixtures thereof; and
 - b) laundry agents comprising from 5% to 100% by weight of deliverable agents, except that said laundry agents do not comprise more than 6% of a mixture of non-deliverable agents containing at least 0.1% isobutyl quinoline, at least 1.5% galaxolide 50%, at least 0.5% musk xylol, at least 1.0% exaltex, and at least 2.5% patchouli oil.
2. The laundry particle according to Claim 1 wherein the laundry agent is a perfume agent.
3. The particle according to either of Claims 1 or 2 further comprising from 0.1% to 50% blocker agent.
4. The particle according to any of Claims 1-3 comprising from 0% to 80% of deliverable agents having ODTs between 10 ppb and 1 ppm, and from 20% to 100% of deliverable agents having ODTs less than or equal to 10 ppb.
5. The particle according to any of Claims 1-4 wherein at least 80% of the deliverable agents have a ClogP value greater than 1.0.
6. The particle according to any of Claims 1-5 wherein at least 50% of the deliverable agents have boiling points less than 300°C.
7. A granular detergent composition comprising:
 - a) from 0.01% to 50%, by weight, of the laundry particle according to Claim 1; and
 - b) in total from 40% to 99.99%, by weight, of laundry ingredients selected from the group consisting of surfactants, builders, bleaching agents, enzymes, soil release polymers, dye transfer inhibitors, and mixtures thereof.
8. A detergent composition according to Claim 7 further comprising from 5% to 80%, by weight, of a detergent builder and from 5% to 80%, by weight, of deterative surfactant.

9. A granular detergent composition according to either of Claims 7 or 8 having a bulk density of at least 550 grams/liter.
10. A detergent composition according to any of Claims 1-9 further comprising a perfume sprayed onto the surface of said detergent granules.
11. A granular detergent composition comprising:
 - a) from 0.01% to 50%, by weight, of the laundry particle according to Claim 4; and
 - b) in total from 40% to 99.99%, by weight, of laundry ingredients selected from the group consisting of surfactants, builders, bleaching agents, enzymes, soil release polymers, dye transfer inhibitors, and mixtures thereof.
12. A granular detergent composition comprising:
 - a) from 0.01% to 50%, by weight, of the laundry particle according to Claim 5; and
 - b) in total from 40% to 99.99%, by weight, of laundry ingredients selected from the group consisting of surfactants, builders, bleaching agents, enzymes, soil release polymers, dye transfer inhibitors, and mixtures thereof.

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FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/14871

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D3/50 C11D3/12 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 28107 A (PROCTER & GAMBLE) 8 December 1994 cited in the application see claims; example 5 ---	1,2,4-12
A	EP 0 149 264 A (UNILEVER) 24 July 1985 see claims ---	1,2,7
A	EP 0 535 942 A (UNILEVER) 7 April 1993 cited in the application see page 3, line 3 - line 26; claims; example 1 --- -/--	1,2,4-8, 11,12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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Date of the actual completion of the international search

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Date of mailing of the international search report

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Grittern, A

INTERNATIONAL SEARCH REPORT

Internat I Application No
PCT/US 96/14871

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 7949 Derwent Publications Ltd., London, GB; Class D25, AN 79-87686B XP002023916 & DD 137 599 A (KAUFMANN D) , 12 September 1979 cited in the application see abstract</p> <p style="text-align: center;">---</p>	1,2,7
A	<p>DATABASE WPI Section Ch, Week 9238 Derwent Publications Ltd., London, GB; Class A97, AN 92-312565 XP002023598 & JP 04 218 583 A (SHOHKOH KAGAKU KENKYUUSHO KK) , 10 August 1992 cited in the application see abstract</p> <p style="text-align: center;">---</p>	1,2
A	<p>DATABASE WPI Section Ch, Week 8951 Derwent Publications Ltd., London, GB; Class A97, AN 89-372973 XP002023917 & JP 01 256 597 A (KAO CORP) , 13 October 1989 see abstract</p> <p style="text-align: center;">-----</p>	1,2,4-7

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International Application No

PCT/US 96/14871

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		CA-A- 2079241	03-04-93
		JP-A- 5209188	20-08-93
		KR-B- 9600197	03-01-96
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